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Review of Treatment Alternatives for Wastes Containing Nonsolvent Halogenated Organics

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16. ABSTRACT

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HAZARDOUS WASTE MANAGEMENT

TREATMENT TECHNOLOGIES FOR HAZARDOUS WASTES: PART V

A Review of Treatment Alternatives for Wastes Containing

Nonsolvent Halogenated Organics

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The Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act direct the Environmental Protection Agency to determine the available treatment technologies for a number of hazardous waste streams, including halogenated organics. If it is determined that existing technology and capacity is sufficient for the safe management of the designated halogenated organic wastes, these wastes will be prohibited from land disposal, effective July 8, 1987. This article summarizes the general characteristics and treatment alternatives for this waste category.

The 1984 RCRA Hazardous and Solid Waste Amendments require that EPA publish regulations banning all hazardous wastes from land disposal unless it is found that land disposal of particular wastes will be protective of human health and the environment as long as the wastes remain hazardous. The amendments allow variances and extensions of the ban effective dates. Before these dates, EPA must identify acceptable alternative technologies and determine the available capacities of these technologies for all RCRA hazardous wastes which could be banned from land disposal.

Halogenated wastes are defined as any listed hazardous waste containing halogenated organic compounds at concentrations equal to or greater than 1000 mg/Kg (1000 ppm by weight).[1] The RCRA land disposal prohibition is scheduled to take effect on July 8, 1987, unless EPA studies show that there is insufficient capacity or alternative technology for managing these wastes. This article discusses characteristics and management of nonsolvent halogenated wastes. Solvent treatment technologies were discussed in an earlier article in this journal.[2]

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Waste Characteristics, Generation and Management

Many halogenated organic wastes exhibit high toxicity, mobility, persistence, and bioaccumulation. The EPA previously promulgated requirements under the RCRA which restrict the land disposal of ignitable, reactive, incompatible, and liquid wastes including solvents, explosive wastes and reactive cyanides (DOXX wastes). The codes for the RCRA-listed wastes are shown in Table I.[3] (The original 13 nonspecific FXXX process wastes are omitted from this table). The DOXX wastes that contain halogenated organics are the pesticide wastes DO12 through DO17. The KXXX wastes are the wastewater treatment sludges from wood preserving processes (K001), pigment production (K002 through K008), still bottoms and residues from various chemical processes.

Of the 446 RCRA-listed wastes, approximately one-fourth (120) of these RCRA wastes contain nonsolvent halogenated compounds. There are 71 halogenated organic compounds included in the 120 RCRA wastes. Over 90 percent of the halogenated wastes which would be affected by the land disposal restrictions have chlorine as a constituent.[4]

An estimated 24.2 million gallons of nonsolvent halogenated wastes were generated in 1981.[5] The quantities of these wastes by subgroup are shown in Table II. Chemical wastes from specific processes (KXXX) constitute about one-half of the total volume. The largest quantity reported by individual waste code was K001 (2.9 million gallons).

As indicated in Table III, about 3 million gallons of nonsolvent halogenated wastes were land disposed in 1981, primarily by deepwell injection and land-filling.[5]

Information shown in Table IV from the 1981 National Survey respondents indicates that about 31 million gallons per year of halogenated organic wastes are being treated.[5] This figure compares well with the annual generation estimate of 24.2 million gallons per year. There is some double counting in the estimate for wastes that are both stored and treated.

Waste Treatment Alternatives

There are many factors to consider in determining the appropriate treatment for an halogenated waste. Physical form of the waste and its chemical constituents are two of the more important factors.

Table I. RCRA-listed wastes containing halogenated organic compounds (HOC).

Waste category[a]	Total number listed in Part 261	Total number containing HOCs (%)	Listing of specific hazardous waste codes containing one or more HOCs
DOXX	17	6 (35)	D012, D013, D014, D015, D016, D017
KXXX	76	27 (36)	K001, K009, K010, K015, K016, K017, K018, K019, K020, K021, K028, K029, K030, K032, K033, K034, K041, K042, K043, K073, K085, K095, K096, K097, K098, K099, K105
PXXX	107	23 (21)	P004, P017, P023, P024, P025, P026, P027, P028, P033, P035, P036, P037, P043, P050, P051, P057, P058, P059, P060, P090, P095, P118, P123
UXXX	233	6[illegible]6)	U006, U017, U020, U023, U024, U025, U026, U027, U029, U030, U033, U034, U035, U036, U038, U039, U041, U042, U043, U044, U045, U046, U047, U048, U049, U060, U061, U062, U066, U067, U068, U072, U073, U081, U082, U097, U127, U128, U129, U130, U132, U138, U142, U150, U156, U158, U183, U184, U185, U192, U207, U212, U224, U230, U231, U232, U233, U235, U237, U240, U242, U243, U246, U247
Totals	433	120 (28)	

[a] DOXX—characteristics of EP toxicity; KXXX—specific process wastes; UXXX and PXXX—discarded commercial or off-specification chemical products, manufacturing intermediates.

Information describing the chemical and physical properties of the RCRA halogenated wastes displays wide variations. For example, a K001 waste may contain pentachlorophenol and naphthalene concentrations as low as a few parts per million (ppm) to as high as 20 percent.[6] In this context, the waste's physical form usually is the key determinant in the selection of a treatment technology. For instance, sludges would not be subjected to carbon adsorption and would require preliminary treatment before they could be incinerated in a liquid injection incinerator. The waste treatment options are categorized as either preliminary or final in the following discussions.

Preliminary Treatment

Many of the liquid halogenated waste streams will require pretreatment prior to final treatment. The general processes which are capable of pretreating liquid wastes are phase separation (filtration, sedimentation, centrifugation), component separation or segregation of single-phase aqueous wastes, and chemical transformation (neutralization, precipitation). Liquid and solid organic wastes to be incinerated, e.g. still bottoms, may need to have particle sizes or viscosity reduced prior to any blending to adjust the heat content, or to hold the halogen content within a prescribed specification. Many of these pretreatment options are adequately described in the literature cited and do not necessarily apply only to halogenated wastes.

Final Treatment

The principal treatment processes with potential application to nonaqueous and aqueous halogenated organic wastes are given in Table V. Aqueous wastes are defined for this discussion as having water content of 95 percent or higher. Nonaqueous wastes generally will have 50–95 percent or more organic liquids and solids content. A third category consisting of mixed aqueous/organic wastes introduces uncertainty into the choice of treatment. The actual organic/water content will usually determine the appropriate treatment techniques. Both aqueous and mixed aqueous/organic wastes can be treated by liquid injection incineration if blended with other organic liquids having higher heating values. It may be practical in some cases to treat aqueous waste streams by steam stripping, distillation, solvent extraction or evaporation to recover the organics.

Table VI presents an overview of each of the waste treatment technologies as applied to various waste physical forms. The operating principles, applicable wastes, costs, and environmental considerations of the technologies, wastes, and environmental consideration are briefly described in the next sections. A summary of the waste treatment technologies is given in Table VII.

Table III. Estimated quantities of halogenated nonsolvent wastes that are land disposed.

Land disposal option	Total quantity disposed (gal/yr)
Landfill	1,439,782
Deepwell injection	1,590,380
Land treatment	107,068
Surface impoundment	28
Totals	3,137,258

Table II. Annual generation of halogenated organic nonsolvent wastes.

Subgroup	Number of waste codes	Estimated maximum quantity generated (10^6 gal/yr)
Pesticides (i.e. DOXX)	43	7.6
Specific process wastes (i.e., KXXX)	26	12.5
Single constituent waste codes (i.e., PXXX and UXXX)	29	4.1
Totals	98	24.2

Evaporation

Evaporation is the vaporization of liquid from a solution, slurry, or sludge through the application of an energy source. This process is practical when one component is minimally volatile. In some instances, the liquid to be evaporated is water and the technology is used to concentrate the nonvolatile component. In other cases, evaporation

Table IV. National survey projections for treatment of nonsolvent halogenated organic wastes (gal/yr).

Treatment option	Specific process wastes KXXX	Pesticides DOXX	Single constituent waste codes PXXX, UXXX	Total halogenated organics
Treatment in tanks	154,786	14,796,844	17,300	14,968,930
Surface impoundment	14,025,171	0	0	14,025,171
Incineration	1,852,975	185,706	65,352	2,104,033
Other	72,078	0	0	72,078
Totals	16,032,932	14,982,550	82,652	31,170,212

is used to separate solvent from nonvolatile solids, oil, or water as a first step in the reclamation of waste solvent.

The two types of evaporators or separators (usually employed to recover spent solvents) are the scraped surface evaporator and thin-film evaporator. A scraped surface evaporator is designed to facilitate density separation of spent solvent materials. This type of separator is suited for solvent streams with a high concentration of suspended solids and sludges. The thin-film separator operates on the same principle as the scraped surface separator except that a film of liquid material is spread against the vessel wall where it is exposed to heat. The thin-film evaporator may be best suited for reclaiming low boiling point solvents. The five largest recycling facilities in California use thin-film evaporation to reclaim solvents directly or as preliminary treatment.[4] Evaporation technology is described in more detail in a previous *JAPCA* article.[2]

Distillation

Distillation is the vaporization of one or more, usually concentrated, volatile components out of liquid solution. Individual components vaporize in order of their volatility so that relatively pure products result upon condensation. Organic products are purified or volatile chemicals are recovered. Nonvolatile residues of varying solids concentration remain behind in the feed.

Steam distillation is likely the most commonly used technique for recovery of halogenated solvents. Steam distillation is a process in which separation of materials is achieved by using their differences in boiling points. The two general types of simple stream distillation processes differ in the method of steam use, e.g., through coils or direct injection. Stills with steam coils are widely used onsite by operators which do not have high waste demands. Direct injection steam stills are most effectively used on low boiling compounds that are not miscible in water. Batch steam distillation is described in Figure 1.[7]

Thin-film evaporation followed by fractional distillation may also be used to recover spent halogenated materials. Fractional distillation is addressed in more detail in a previous *JAPCA* article.[2]

Liquid Injection Incineration

A liquid injection incinerator consists of a waste atomizing burner injecting a combustible liquid and air into a combustion chamber. Operating temperatures range from 1,200 to 3,000°F and gas residence time ranges from 0.1 to 2.0 seconds.[8] Excess air usage of 20–25 percent or greater is needed for adequate combustion. Typical burner sizes range from 1 to 100 million Btu/h. Auxiliary fuel is required during startup and is usually needed for wastes with heating values of less than 8,000 Btu/lb.

Table VI. Treatability matrix for halogenated nonsolvent wastes.

Treatment alternative	Aqueous streams	Inorganic streams	Organic liquids	Organic solids
Established technologies				
Rotary kiln incineration		X	X	X
Fluidized-bed incineration			X	X
Liquid injection incineration	X		X	
Lime/cement kiln coincineration			X	
Carbon adsorption	X			
Steam stripping	X			
Biological treatment	X			
Evaporation	X		X	
Distillation			X	
Solvent extraction			X	X
Emerging Technologies				
Molten salt incineration			X	X
Plasma arc incineration (pyrolysis)			X	X
High temperature fluid wall destruction		X	X	X
Supercritical water oxidation	X			
UV/ozone treatment	X			
Wet air oxidation	X			
Chemical dechlorination			X	
Chlorinolysis			X	

Table V. Technologies for management of halogenated organic wastes.

Recovery/Reuse	Treatment	Destruction
Evaporation	Dechlorination	Incineration
Distillation	Carbon adsorption	Molten salt
Chlorinolysis	Biological	Plasma arc
Steam stripping	UV/ozonation	High temperature fluid wall
	Wet air oxidation	Lime/cement klin coincineration
	Supercritical water	
	Solvent extraction	

Liquid injection incinerators are usually limited to pumpable liquids and slurries with viscosities of 750 ssu or less and solids contents less than 20 percent. Halogenated organic wastes can be destroyed in these units as long as alkaline scrubbing is used to control acidic offgases. Examples of halogenated wastes destroyed include the pesticide kepone in a pilot-scale plant and hexachlorocyclopentadiene, which was incinerated in a full-scale facility with a resulting 99.99 percent destruction efficiency.[9]

The cost of incinerating a waste in a liquid injection incinerator depends on the chemical constituents present and the waste's heating value. A waste with

Table VII. Summary of existing waste treatment technologies.

Waste category	Land disposed waste volume (gal/yr)	Existing treatment technology	Comment
High chlorine content KXXX wastes	1,673,977 (liquid)	Liquid injection incineration/waste blending/caustic scrubbing	~4,000 Btu/lb
	612,291 (solid)	Rotary kiln incineration	~4,000 Btu/lb
Halogenated aqueous KXXX wastes	0	Filtration/steam stripping/carbon adsorption	
Halogenated aqueous sludge KXXX wastes	23,970	Waste blending/liquid injection incineration	~4,000 Btu/lb
		Rotary kiln incineration	~4,000 Btu/lb
Halogenated high inorganic KXXX liquid wastes	128	Rotary kiln incineration with high efficiency scrubber	~1,000 Btu/lb
		Solidification/land disposal	
Halogenated potential gases	0	Liquid injection incineration/caustic scrubbing	Unknown Btu content
Halogenated potential solids	68,216	Rotary filn incinceration with caustic scrubbing	Assumed ~ 4,000 Btu/lb
Other halogenated organics with inorganic solids	759,274	Rotary kiln incineration with caustic scrubbing	Assumed ~ 1,000 Btu/lb
Total	3,137,860		

a high halogen content will require a caustic scrubber to remove halogen acid gases and also supplemental fuel to improve combustion since chlorinated wastes (for example) typically have lower heating values than nonchlorinated wastes.

Atmospheric emissions will depend on the specific waste being incinerated, but may consist of hydrochloric acid, some ash, and possibly trace metals.

Rotary Kiln Incineration

A rotary kiln incinerator consists of a cylindrical, refractory-lined shell mounted with its axis at a slight incline (less than 5°) and may rotate from 5 to 25 times per hour. The rotational speed, which may range from 1 to 5 ft/min, provides excellent mixing of wastes and combustion air.[10] Normal kiln operating temperatures range from 1,500 to 3,000°F with excess air rates ranging from 140 to 210 percent. Gas residence times can be from 0.4 to 4 seconds while solids residence times can range from 0.5 seconds (for fine particles) to one or more hours (for bulky objects).

Most solids, liquids, and sludges can be handled in a rotary kiln provided that it is equipped with appropriate feed mechanisms. Examples of halogenated wastes that can be incinerated in rotary kilns are:[11]

- chlorotoluene production wastes,
- epichlorohydrin manufacturing wastes,
- PCB wastes in capacitors, and
- nitrochlorobenzene tars.

High destruction efficiencies in full-scale rotary kilns have been reported for hammermilled PCB-containing capacitors and vinyl chloride sludges.[8]

Capital costs for rotary kilns are affected by design temperature (i.e., refractory requirements), waste form, and feed and ash handling systems while operating costs are influenced by halogen or fusible ash content in the waste, auxiliary fuel requirements, and amount of scrubber chemicals needed.

Stack gas emissions are highly dependent on specific waste composition and physical form.

Fluidized-Bed Incineration

A fluidized-bed incinerator (FBI) is also applicable to the destruction of halogenated organic waste streams. This type of unit consists of a vessel in which inert granular particles are fluidized by a low velocity air stream which is passed through a distributor plate below the bed. An FBI consists of a windbox, through which combustion air is introduced to the reactor; a reactor zone, containing a bed of sand, waste injection nozzles, and sand loading and removal nozzles; and the freeboard section at the top of the unit where bed material trapped in the gas stream can separate out before being exhausted.

Operating temperatures range from 1,300 to 2,100°F, gas residence times are usually several seconds, and excess air rates are normally 40 percent or less. Heat release rates are quite high, ranging from 100,000 to 200,000 Btu/h-ft^3.

Fluidized-bed incinerators have been used to destroy a wide range of waste materials including the following:[12]

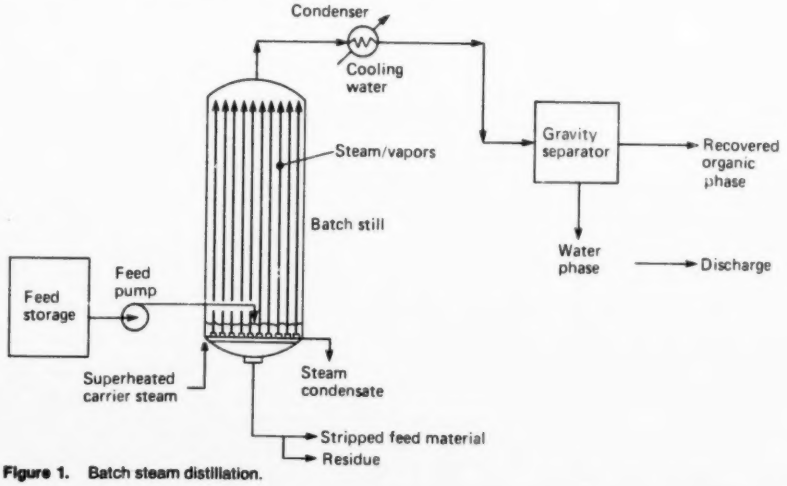

Figure 1. Batch steam distillation.

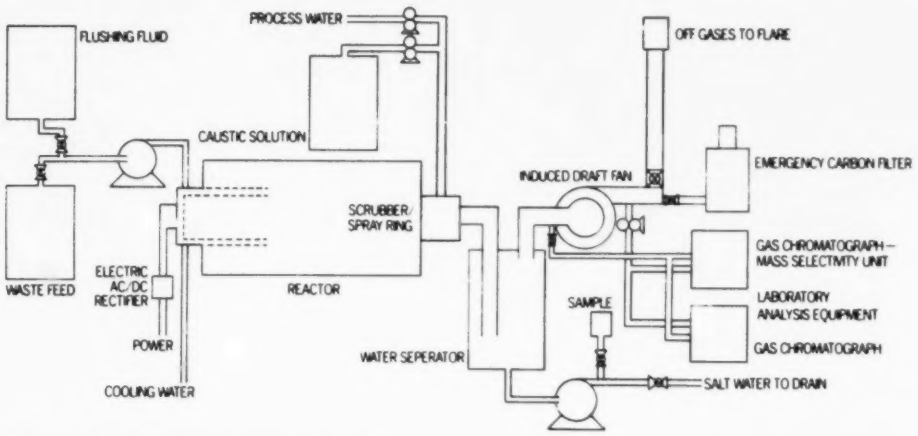

Figure 2. Process schematic of PSI pyrolysis unit.

- municipal sewage sludge,
- low quality fuels (i.e., wood waste, anthracite culm, etc.),
- pulp and paper effluents,
- food processing waste,
- refinery wastes,
- radioactive wastes, and
- miscellaneous chemical wastes.

Polyvinyl chloride and chlorinated solvent wastes have been burned in fluidized beds.[3] High destruction efficiencies, (99.9 percent) have been shown for chlorinated compounds such as 1,1,1-trichloroethane, trichloroethylene, perchloroethylene, and freon. Because of the potential for hydrogen chloride emissions, alkaline bed materials such as dolomite or limestone are usually employed.

One of the main operating costs for FBIs is for auxiliary fuel. One reason for this is that the fuel required for startup is higher than for other types of incinerators because the heat capacity of the fluid bed is much greater. Other costs are highly variable and dependent upon the waste type.

Effluent emissions can be different from other incinerators in that a portion of the bed materials is occassionally withdrawn and discarded. This material will consist of ash from the waste plus some sand. While particulate emissions can be higher than other units, NO_x emissions are usually lower because of lower operating temperatures.

Molten Salt Incineration

This process is based on the use of a molten salt such as sodium carbonate as a heat transfer and reaction medium. In the process, waste material along with air is added below the surface of the bed so that any gases formed during combustion are forced to pass through the melt. Reaction temperatures in the bed range from 1,500 to 2,000°F and residence times are typically 0.75 seconds. Acidic gases such as HCl produced by burning halogenated

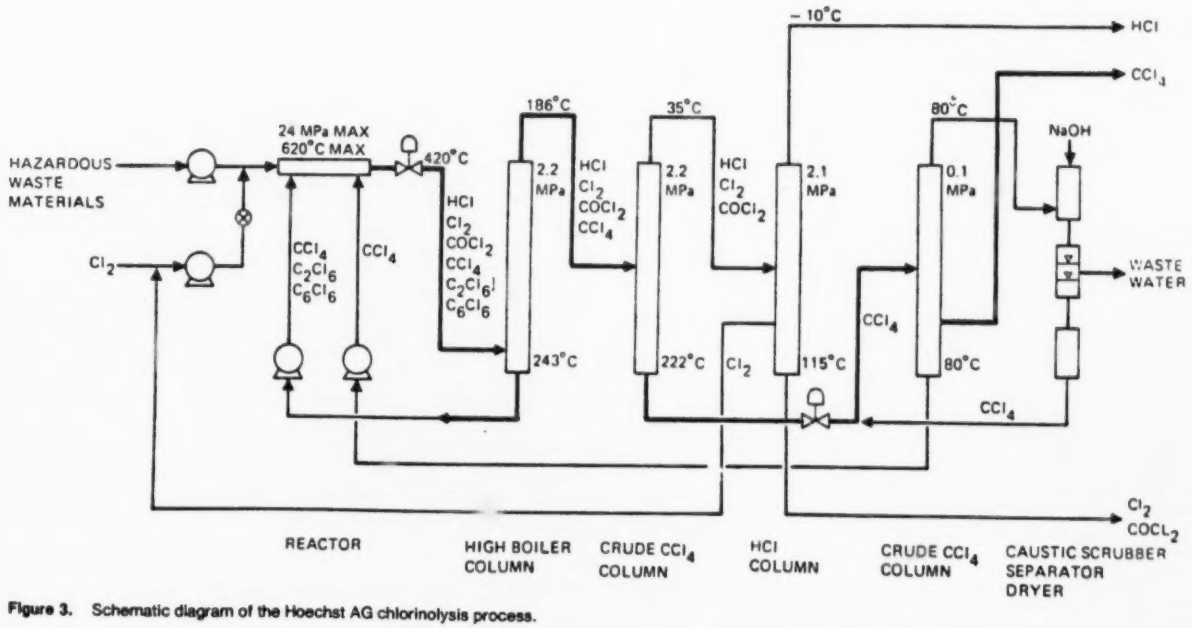

Figure 3. Schematic diagram of the Hoechst AG chlorinolysis process.

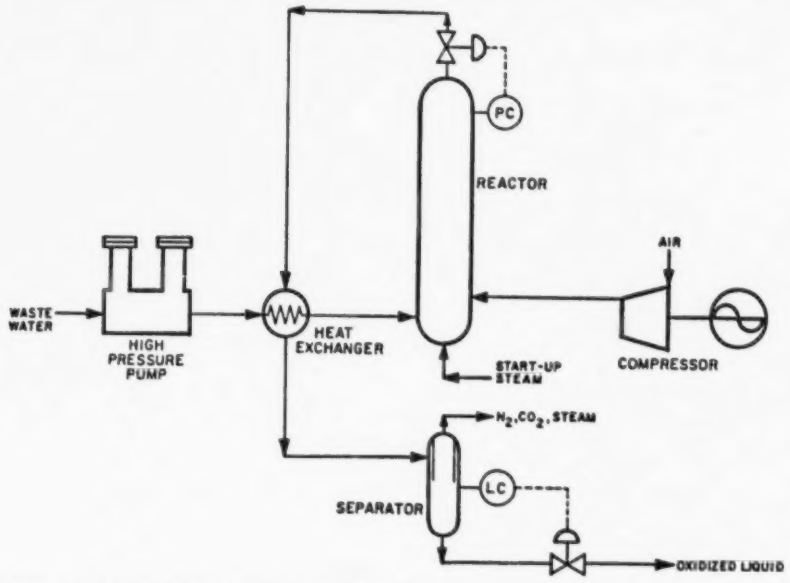

Figure 4. General schematic—Zimpro wet air oxidation.

organics are neutralized by the alkalinity in the bed. The neutralization of acidic gases results in the formation of other salts that can change the fluidity of the bed and, hence, require frequent replacement of the bed material.

Because of the potential for acidic gas scrubbing within the melt, halogenated wastes have received much attention in the testing of this process. Liquid halogenated wastes that have been combusted in bench or pilot scale units include chlorodane, 2,4-D, chloroform, trichloroethane, perchloroethylene still bottoms, and PCBs, while solids incinerated include hexachlorobenzene.[13]

One of the major factors influencing costs is the frequency of bed replacement. When the salt bed reaches 20 percent impurities by weight, it is withdrawn for reprocessing or disposal; for a high chlorine content wastes, the replacement of the bed may be as high as one pound of bed per pound of waste destroyed.

Because no full scale molten salt incinerators have been built, costs are not available, although auxiliary fuel requirements should be relatively low.

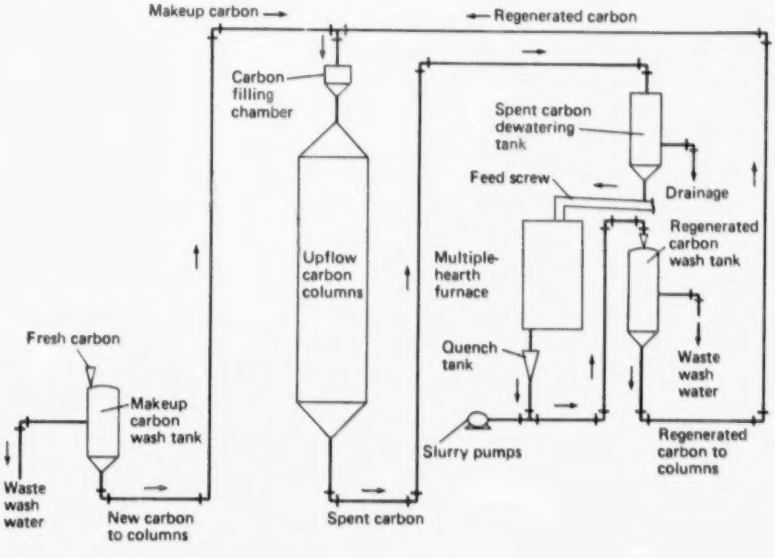

Figure 5. Carbon regeneration diagram for upflow columns.

Gaseous emissions from molten salt incinerators generally contain low levels of halogens, NO_x, and trace metals and relatively high (2.4 percent) concentrations of carbon monoxide when incineration is carried out at low temperatures.[14] Other process effluents include spent molten salt that may contain sulfates, phosphates, chlorides, ash, and heavy metals. This spent material can either be reprocessed or disposed.

Plasma Arc Incineration

The plasma arc pyrolysis process (see Figure 2) is based on the concept of reducing (pyrolyzing) waste molecules to the atomic state using a thermal plasma field.[15] The system uses very high intensity energy at temperatures approaching 10,000°C to break bonds of hazardous waste chemical molecules down to the atomic state. A colinear electrode assembly is used to produce the electric arc. Dried low pressure air is used as the medium through which the electric current passes. Air molecules are subsequently ionized forming the plasma field. Upon return to the ground state, the ionized molecules emit ultraviolet radiation.

Hazardous waste mixtures are injected into the field and interact with the plasma field. This interaction results in a reducing mechanism in which the molecules are atomized. Upon cooling, simpler molecules such as hydrogen, carbon dioxide, carbon monoxide, hydrogen chloride, and other minor matrix compounds such as acetylene and ethene are formed.

The plasma pyrolysis unit consists of a liquid waste feed system, pyrolysis reactor, caustic scrubber, flare, and online analytical equipment. Gaseous effluents from the reactor pass through a caustic venturi type scrubber followed by a flare for final gas cleanup. This unit, operated by Pyrolysis Systems, Inc. (PSI), has a nominal capacity for 4 kg/min (55 gal/h). Gas flow rates at this operating level are on the order of 5–6 m^3/min prior to flaring operations and 3,600 m^3/min after the flare at actual conditions.

Preliminary tests on the pilot unit showed a destruction and removal efficiency of greater than 99.99 percent for PCB waste and other waste streams containing trichlorobenzene. However, the mobile pilot unit has experienced some operational problems and has not been able to sustain long-term endurance runs.

The major cost for the plasma arc unit would be the electrical energy which must be supplied to produce the electric arc, which is on the order of 0.84 kWh per kg of waste fluid.

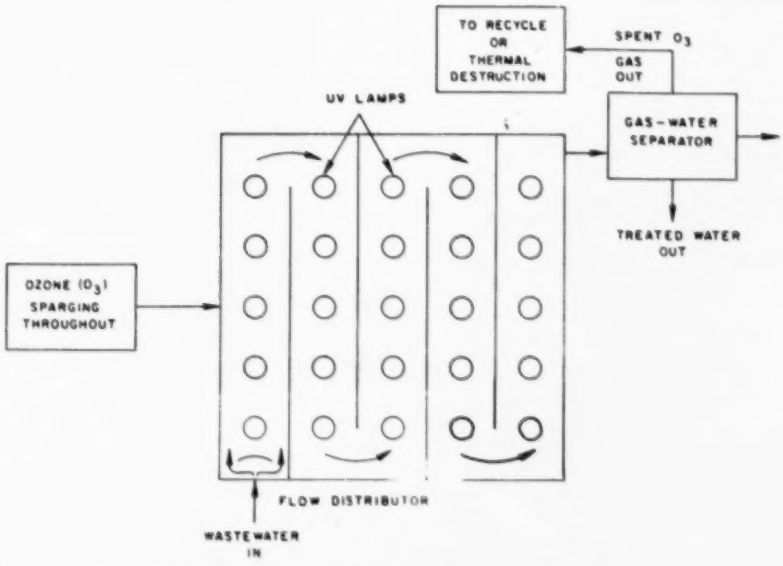

Figure 6. Schematic of Ultrox UV/ozone treatment system.

Effluent off gases from this system should present no problems when no operating difficulties are experienced; however these gases as well as the discharged scrubber water should be closely monitored.

High Temperature Fluid Wall Reactor

The HTFW reactor was originally developed by Thagard Research of Costa Mesa, California, while the J.M. Huber Corp. of Borger, Texas has developed proprietary modifications. This system, also referred to as the Advanced Electric Reactor, is a thermal destruction device which employs radiant energy provided by electrically treated carbon electrodes to heat a porous reactor core. Process characteristics for this system were discussed in a previous issue of *JAPCA*.[16] While the process appears mainly applicable to soils contaminated with dioxin wastes, other potential applications include PCBs and heavily halogenated hydrocarbons.

Lime/Cement Kiln Coincineration

Combustion of hazardous wastes in lime or cement kilns is an attractive waste treatment alternative. The cost of fuel for these processes can account for 50 percent of operating costs and so the use of hazardous waste as a supplemental fuel is a desirable option.

A cement kiln is basically a large rotary kiln about 300 feet long and 10–20 feet in diameter into which raw materials are fed countercurrent to combustion gas flow. The kilns most suitable to hazardous waste destruction are wet process kilns, which utilize a 30 percent water slurry feed.

Burning of chlorinated wastes in a cement kiln is especially attractive because the clinker product formed is highly alkaline and thus acts as a scrubber to remove acid gases produced during combustion. Most liquid halogenated waste streams should be capable of high efficiency destruction. The most desirable wastes would be high Btu, low chlorine residual streams. Generally, chlorine content should be 3 percent or less of the total fuel (fuel oil plus hazardous waste). Halogenated compounds which have been successfully destroyed in cement kilns include PCBs, carbon tetrachloride, hexachlorocyclopentadiene, chlorobenzene, chlorotoluene, and chloroform.[3]

Chemical Dechlorination

Several chemical dechlorination processes have been developed in recent years, each using a sodium reagent to strip chlorine atoms from highly chlorinated molecules such as PCBs to form sodium chloride and an inert polypropylene sludge. These processes are fairly similar and are based on a process developed by Goodyear Tire and Rubber Co. The Goodyear process involves the use of tetrahydrofuran to dissolve molten sodium and naphthlene with the resulting sodium naphthalide capable of stripping chlorine atroms from the waste molecules. The other processes that have been developed (i.e., APEG, Acurex, and PPM) substitute proprietary reagents for naphthalene since naphthalene is a priority pollutant.

Chemical dechlorination processes have been designed primarily for the treatment of oil contaminated with PCBs (500–5,000 ppm).[17] These processes should be applicable to most types of highly halogenated compounds. For example, the sodium polyethylene glycol reagent used in the APEG process has also been used on such halogenated compounds as hexachlorocyclohexane, hexachlorobenzene, tri- and tetrachlorobenzenes, and pentachlorophenol.

Chlorinolysis

Chlorinolysis (also referred to as chlorolysis) is a manufacturing process capable of using organochlorine wastes as feedstock materials for production of perchloroethylene, trichloroethylene, or carbon tetrachloride.[18] The process is essentially a pyrolysis reaction in which excess chlorine is added to the feedstock at temperatures of 400–600°C so that the carbon-carbon bonds of the hydrocarbons can be broken and the molecular fragments can react with chlorine to form chlorinated hydrocarbons. Several companies have developed processes capable of converting C_1 to C_3 hydrocarbons to chlorinated solvents. Hoechst-Unde of Germany has patented a process for converting C_1 to C_6 organochlorine compounds, and thus appears to be the only chlorolysis process capable of handling aromatic feedstocks such as hexachlorobenzene.[10] The Hoechst-Unde process (shown in Figure 3) consists of a nickel tube reactor surrounded by a stainless steel jacket and a series of distillation columns for separation of reaction products.

Suitable organochloride wastes that could be used as feedstocks for this process include residues from production of vinyl chloride monomer, chloromethanes, allyl chloride, perchloroethylene, and benzene chlorination. Potential waste feedstocks should be free of sulfur (because it is corrosive to nickel), nitrogen and phosphorous (because of side formation of trichlorides), and oxygen (because of possible phosgene formation).

The economic feasibility of the chlorinolysis process is mainly dependent on the market selling process of carbon tetrachloride. Other costs vary depending on how much chlorine is required.

Air and water discharges from this process are not expected to be significant.

Wet Air Oxidation

Wet air oxidation involves the aqueous phase oxidation of organic or inorganic materials at high temperature and pressure. A major advantage of this process over conventional incineration is that water in the waste stream is kept in the liquid state at the high operating pressures (typically around 1,500 psi). A schematic diagram of the Zimpro process is shown in Figure 4. Operating temperatures range from 175 to 320°C while pressures range from 300 to 3,000 psi. Residence times may range from 1 hour or longer for difficult to destroy wastes.[19]

Waste is pumped into the reactor along with compressed air or pure oxygen and is preheated by the hot effluent. Two types of reactors are used: a bubble tower reactor (the more common) and a stirred tank cascade reactor. The bubble tower is a vertical reactor wherein mixing is affected as a result of air bubbles rising through the reactor.

Generally, wet air oxidation is applicable to wastes that are too dilute to incinerate and yet too toxic for biological treatment. Chlorinated aliphatics and halogenated aromatics are capable of destruction by wet air oxidation. Compounds such as chlorobenzenes, chlorinated pesticides, and PCBs are resistant to the process, however.

For dilute streams, wet air oxidation units generally have higher capital, but lower operating costs than conventional incineration processes. The major operating cost is energy consumption by the compressor.

Typically, 80 percent of the waste influent is oxidized to carbon dioxide and water, while the remainder consists of partially treated material. Thus, further treatment (i.e., biological) may be necessary.

Carbon Adsorption

Carbon adsorption is used to remove soluble organics from wastewaters through contact of the waste stream and activated carbon, passage of the purified stream, and disposal, destruction, or regeneration of the spent carbon. The two principal carbon contacting systems are downward through the bed (pressure or gravity flow) and upflow through a packed or expanded bed. An upflow system along with associated carbon regeneration hardware is depicted in Figure 5.[3]

An alternate means of using activated carbon consists of adding powdered carbon directly to biological treatment effluent in a contacting basin. After sufficient contact time, the carbon is recovered by settling and/or filtration.

Activated carbon adsorption is applicable to treatment of dilute aqueous wastes. Wastewater should be pretreated, however, to remove suspended solids, oil and grease. Temperature and pH are also important on a compound specific basis. In general, nonpolar, high molecular weight organics with limited solubility are preferentially adsorbed and branched chain compounds are more adsorbable than straight chain compounds. Chlorinated pesticides (i.e., chlordane and heptachlor) and chlorinated aliphatics (i.e., trichloroethane) have been effectively removed from wastewaters using activated carbon.[20]

The prime factor affecting the economics of activated carbon treatment is the carbon exhaustion rate. The two main emission streams are spent carbon and treated effluent. If the carbon consumption rate is more than 400 lb/day, it is usually regenerated. This can be done either chemically or thermally, although thermal regeneration in a rotary kiln, multiple hearth, or fluidized-bed furnace is more common.

Steam Stripping

Steam stripping involves the heating of a wastewater stream to its boiling point and then forcing steam through the water to remove hazardous organic compounds by volatilization. Countercurrent flow is generally used to promote gas-liquid contact, thus allowing soluble gaseous organics from the liquid waste to be continuously exchanged with molecules within the stripping gas. Molecular transfer is highly dependent on wastewater temeprature and the vapor pressure of compounds in the waste stream.

Steam stripping is applicable to wastewaters containing organics with low water solubilities (usually less than 1,000 ppm) and low boiling points. Waste streams should contain less than 10 percent volatile organics and less than 2 percent suspended solids.[21] Examples of halogenated organic compounds removed by steam stripping are chlorobenzene, methylene chloride, chloroform, carbon tetrachloride, and hexachloroethane.

Annual operating costs for a steam stripper are a function of the amount of steam required and whether the organics removed are recoverable or need to be incinerated. Highly volatile constituents emitted by the stripper may require further scrubbing or incineration while the stripped water stream may require further treatment such as carbon adsorption.

Biological Treatment

Biological treatment involves the degradation of organic compounds by microorganisms, the primary purpose being to reduce the biochemical oxygen demand (BOD) of the waste stream. Suspended growth systems, such as activated sludge units, aerated lagoons, and anaerobic digesters consist of microorganisms suspended in the wastewater mixture. Fixed film processes, such as trickling filters and rotating biological contactors, involve a fixed surface upon which the microorganisms grow. Biological systems can be either aerobic or anaerobic. Anaerobic units use bacteria that can only exist in an environment devoid of oxygen. These units have slower reaction rates and much less sludge production than aerobic systems.

Because toxic organics normally degrade very slowly, it has been suggested that fixed film processes such as rotating biological contactors may provide the best means of treating dilute hazardous wastes because microbial population retention is very high in these units.

For the most part, only dilute aqueous waste streams with an organic content of less than 1 percent are amenable to biological treatment. Some halogenated organics that have been successfully treated include chlorobenzene, carbon tetrachloride, chlorodibromoethane, methyl chloride, and 2,4,6-trichlorophenol.

For dilute aqueous waste streams, biological treatment is one of the most economical alternatives. The major energy costs are for aeration, although with anaerobic systems this cost is eliminated.

Nondegradable pesticides or other organics may be unaffected by biological treatment and, thus, a finishing process such as activated carbon adsorption may need to be employed.

UV/Ozonation

This is an oxidation process in which the wastewater is simultaneously subjected to ultraviolet radiation and ozone. The use of ultraviolet radiation enhances the oxidation power of the ozone thereby increasing the reaction rate and oxidation efficiency. One type of UV/ozonation reactor uses compartments created by baffles with cylindri-

cal UV lights placed vertically at equal distances along the flow path, as illustrated in Figure 6. Another design, called the multistage reactor, uses several reactors in series.

UV/ozonation is generally restricted to wastewaters with 1 percent or less of an organic contaminant. Since ozone is a nonselective oxidant, the waste stream should contain primarily the compound of concern. Halogenated organics that can be treated with UV-ozone include aldrin, chlorinated phenols, dieldrin, endrin, ethylene, dichloride, kepone, methylene chloride, PCBs, and pentachlorophenol.[3]

The major costs for this type of system are the reactor and ancillary ozone and UV generation equipment.

Supercritical Water Oxidation

Supercritical water oxidation is a liquid phase oxidation process for destroying aqueous wastes containing high organic concentrations.[22] Water in its supercritical state (pressure greater than 218 atmospheres and temperature greater than 374°C) is able to achieve rapid and complete oxidation of organic compounds. Organic compounds become completely soluble and inorganic salts only sparingly soluble.

This process was described in a previous issue of *JAPCA*.[16] The process is mainly designed to treat wastewaters with organic concentrations in the 1 to 20 percent range. These types of wastes are too dilute for economical incineration and too concentrated to treat using activated carbon. Halogenated compounds that have been treated with this technique include 1,1,1-trichloroethane, ethylene dichloride, *o*-chlorotoluene, 1,2,4-trichlorobenzene, and PCB 1254.[13]

The major capital cost associated with this process is the air compressor, thus the prime factor to consider is oxygen throughput.

Solvent Extraction

Solvent extraction is a process whereby a dissolved or adsorbed substance is transferred from a liquid or solid phase to a solvent that preferentially dissolves that substance. When the waste to be treated is a liquid (often water) the process may be called liquid-liquid extraction, the substance transferred is the solute, the treated effluent is referred to as the raffinate and the solute-rich solvent phase is called the extract. For the process to be effective, the extracting solvent must be immiscible in the liquid and differ in density so that gravity separation is possible and there is minimal contamination of the raffinate with solvent.

Solvent extraction can be performed as a batch process or by the contact of the solvent with the feed in staged or continuous contact equipment. The solvent and the wastewater are agitated in one vessel (the mixer) and then transferred to another vessel (the settler) where the phases are separated by density differences. This operation can occur more than once so that there are multiple mixer-settler stages. Another option, which is depicted in Figure 7 is continuous countercurrent contact in a vertical column such as a spray tower, packed tower, or sieve plate tower.

Solvent extraction is a limited technology in that it is almost always necessary to further treat the raffinate and/or the extract. This technology is typically used when it is not economical or possible to use more standard technologies. The removal efficiency of solvent extraction depends on the solvent, the constituent to be extracted, soil properties if a constituent is being extracted from soil, the liquid containing the constituent, and the unit operation design. Typical removal efficiencies vary from 80 percent to close to 100 percent.

It is often possible to reuse the solvent in the solvent extraction process. This is accomplished by using a distillation column to remove the extracted solute molecules from the solvent in a concentrated form and then reusing the distilled solvent.

In addition, the cost of solvent extraction is relatively high. The high cost of solvent extraction results from initial solvent costs, further treatment of the extract, such as distillation, and disposal costs of the extracted constituents.[23]

Summary

Not all of the processes discussed here have been fully demonstrated. A summary of existing technologies is presented in Table VII for the waste categories currently estimated to be subject to land disposal.

There is much that remains to be learned about the characteristics of the RCRA-listed halogenated organic wastes. There also is a need for continued research and development of treatment technologies applicable to nonsolvent halogenated organics. EPA is currently conducting treatment studies of this and the other waste categories scheduled for land disposal restrictions. The data from these studies will contribute to the determination of the adequacy of available treatment options.

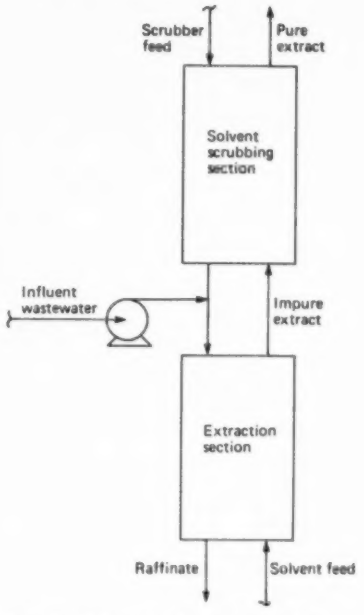

Figure 7. Schematic of solvent extraction.

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Notice. This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Chemical Manufacturers Association

1984 Hazardous Waste Survey

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This paper discusses the Chemical Manufacturers Association's 1984 survey of the chemical industry's hazardous waste management practices. The survey data include a breakdown of how the industry's hazardous wastes are managed, detailing generation, treatment and disposal, and cover 725 plants in 81 companies. The 1984 survey is the third CMA hazardous waste survey, and the paper discusses resultant waste treatment trends from 1981–1984, the period covered by previous surveys. A total of 278.5 million tons of hazardous waste was treated and disposed by survey respondents. Of this, 276.8 million tons was hazardous wastewater and 1.7 million tons was solid hazardous waste. The survey solid hazardous waste total was projected to the entire industry (Standard Industrial Code 2800) and is estimated at 6.9 million tons. The survey showed continued decreasing trends in hazardous waste generation in the chemical industry. It demonstrated changes in hazardous waste management practices, with decreased use of landfills and increased incineration of the solid wastes that are generated.

The Chemical Manufacturers Association (CMA) has surveyed its members' hazardous waste management practices annually since 1981. This paper reports the results of the 1984 survey as well as trends in these practices over the four year period. The 1984 survey was conducted by CMA and Engineering Science.

The survey population is CMA member companies. CMA is a nonprofit trade association whose member companies represent more than 90 percent of the productive capacity of basic industrial chemicals in this country. Eighty one companies, or approximately 50 percent of CMA's members responded to the survey in 1984. The

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